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STEAM DISTILLATION STUDIES FOR THE KERN RIVER FIELD

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Abstract

The interactions of heavy oil and injected steam in the mature steamflood at the Kern River Field have been extensively studied to gain insight into the effect of steam on compositional changes of oil during the recovery process and to provide input for compositional thermal simulation. Steam distillation behavior of this 13 °API California oil between 300 and 500 °F under a variety of process conditions, along with extensive analysis of distilled hydrocarbons were incorporated to give a more in depth description of what is happening to the oil and what changes are occurring in the distillates and produced oil. This information was further integrated with analysis of the field distillate, 'casing blow,' to describe what is happening in the field. The results show that steam distillation is temperature dependent and is more important than originally thought. The data developed in this study is a basis for improvement of numerical thermal models with potential for better designed steamfloods and reservoir management. The results may also impact certain logging techniques used in steamfloods and possible heavy oil upgrading techniques.

Kern River oil is more than 10% distillable at 300 °F and 15 % distillable at 400 °F in dynamic laboratory steam distillation tests at steam throughputs of 4 times the initial volume of oil. Distillate physical properties of density, viscosity, molecular weight, and hydrocarbon composition of the distillates changed significantly. Distillate density, viscosity, and molecular weight properties increased in value with increasing steam throughput, and at higher temperatures. This information is important in the tuning of equations-of-state, including hydrocarbon-water interaction parameters for compositional thermal simulation.

Analysis of the field distillate, 'casing blow,' showed properties similar to laboratory distillates at low steam throughputs. The observation of a light field distillate production in a mature steamflood compared to laboratory measurements implies that the casing system temperature is a major controlling factor in 'casing blow' composition and quantity.

Background

The phase equilibrium behavior of reservoir fluids is an important phenomenon in petroleum production, particularly in enhanced oil recovery processes. However, phase behavior for heavy oils (< 15 ° API) under steamflood has generally been felt to be either unimportant or to be a minimal effect to be neglected.¹ A major question exists about whether or not the phases and fluids in a steamflood are in equilibrium. Proper modeling of a reservoir production process would be expected to include knowledge of the phases and their equilibrium compositions. In heavy oil, devoid of significant C₁ - C₆ composition, it has been sufficient in previous practice for steamflood modeling purposes to treat the oil as a dead oil or as a non-volatile phase. A history match numerical study² of steamflood performance in the Kern River Field treated the oil as non-volatile, and was conducted without the inclusion of hydrocarbon compositional effects.

Through the classic works of Willman et al.³, Volek and Pryor⁴, and Closmann and Seba⁵ steam distillation has been shown to be an important component mechanism in the overall steamflooding process.⁶⁻¹⁰ The practical limit of how much of a reservoir fluid can be distilled, is obtained in dynamic steam distillation experiments developed by Wu and Brown^{11, 12}, extended by Hseuh, Hong, and Duerksen^{13, 14}, and refined by Wu et al.^{15, 16} This body of work demonstrates that steam distillation is an operative mechanism in laboratory models, but it has been difficult to translate this to a quantitative contribution to the field steamflooding recovery process.

Laboratory steam distillation experiments have generally been conducted as dynamic tests, that may or may not be near equilibrium. Experiments near equilibrium with extensive analysis of the phases will yield values for the vapor-liquid equilibrium (VLE) ratios (K-values), another way of assessing the importance of compositional changes in steamflooding. A major recent steam distillation study by Northrup and Venkatesan¹⁷ has been completed on the South Belridge oil.

Compositional data has recently been reported¹⁸ for simple distillation and laboratory steamfloods of oils in the range 13 - 33 °API, including Kern River oil. The current report is an extension of that work to include analyses of produced field samples for the Kern River steamflood.

Compositional reservoir simulators demand greater emphasis on obtaining more in-depth crude oil compositional data, to be used as input into an equation-of-state (EOS) or to calculate equilibrium ratios, K-values. The present work establishes laboratory data to facilitate such efforts.

Laboratory vaporization and steam distillation tests are vital to the understanding of the steamflood mechanism. This partnership of EPTD and TAMU has resulted in the most extensive examination of the steam distillation behavior of one heavy crude oil. Steam distillation of crude oil in petroleum reservoirs has been recognized as one of the major mechanisms responsible for high oil recovery by steam flooding. An appreciable amount of incremental oil^{19,20} could be recovered by steam flooding due to steam distillation depending on the composition of the crude oil. The steady growth of commercial thermal recovery projects has created a need for basic data on phase equilibria of water and hydrocarbons ranging from methane to high boiling-point fractions. Current mathematical compositional reservoir simulators use the results of 2-phase flash calculations by equations of state (EOS) or use 2-phase K-value tables to account for hydrocarbon/water/vapor separation.

Water is ubiquitous in petroleum reservoirs and recovery systems. Therefore, the effects of water on the hydrocarbon separation process are needed by the petroleum industry, for predicting the effects of steam distillation and the phase behavior of hydrocarbon/water systems. Three-phase K-values that account for the effects of steam distillation would be very useful in thermal reservoir simulation studies since they greatly increase the accuracy and reliability of thermal simulators.

The EOS approach and table look-up for 2-phase K-values are applied in thermal numerical simulation models, even though they do not fully represent 3-phase separation (steam distillation). A three-component system approximation was used by Coats and Smart²¹ to incorporate steam distillation effects by adding water as a component in the vapor phase. The compositional variations due to steam distillation cannot be fully described by Coats' model. A difficulty in this model is the lack of 3-phase laboratory steam distillation data for high-temperature and high-pressure conditions. Recent work by Beladi,^{22,23} Wu,²⁴ Lanclos,²⁵ Forero,²⁶ and Lolley^{27,28} has begun to show how to treat this problem.

The goal of this research is to obtain 3-phase laboratory steam distillation data to better understand the effects of water and its vapor on the hydrocarbon separation processes at high-temperature and high-pressure conditions. This includes the investigation on both the pure hydrocarbon component/water systems and crude oil/water systems. The 3-phase equilibrium ratios or K-values determined from these laboratory investigations are necessary to accurately describe the effects of steam distillation in mathematical reservoir simulation.

Experimental

Steam Distillation Cell and Procedures. In order to describe the existing laboratory procedures, Fig. 1 is presented. This experimental set-up was used to perform three different types of tests:

1. Static system pressure test (SPT).
2. Dynamic distillation test (DDT)
3. Stage-wise isochoric distillation test (SWID)

The experimental apparatus was composed of an injection assembly (Ruska pumps and the gas bottles), a distillation cell assembly, a withdrawal assembly (condenser, separator) and an automation/data acquisition assembly. The steam distillation apparatus has been extensively described elsewhere.²²

Static system pressure tests (SPT). Static system pressure tests were run for hydrocarbons (HC) in the presence of water phase (3-phase, VLL equilibria) and in absence of water (2-phase, VL equilibria). These tests were performed on every sample to obtain the system pressures of HC/ water mixtures, and were used as an indication of equilibrium conditions in distillation tests. It was important to have the static pressure data to insure that equilibrium or near equilibrium conditions are reached for SWID tests. The results of these tests can also be used to tune the EOS approaches.

Dynamic distillation tests (DDT). Dynamic distillation tests were performed to investigate the effect of steam injection-rate on the steam distillation yields. This testing procedure was primarily used to obtain the maximum steam distillation yield.

Stage-wise isochoric distillation (SWID) tests. The SWID test is a stage-wise distillation test conducted in a constant volume cell (isochoric). At each stage the system is brought to equilibrium before the distillate sample is removed from the vapor phase. We performed two types of SWID tests:

SWID-1) This test was conducted under stepwise increase of temperature for each stage. The equilibrium was reached between the stages. After the equilibrium was reached, distillate sample is removed for compositional analysis of the vapor phase. From the volumes of the distillate and the composition of the hydrocarbon phase, the new over-all composition in the cell was calculated by the mole balance. The remaining components with the calculated overall compositions were used for the next stage of test (at a higher temperature). This method was originally reported as the semi-static test.

SWID-2) This test was conducted at a constant temperature for all stages. Equilibrium is reached between the stages. After equilibrium was reached, distillate sample was removed for compositional analysis of the vapor phase. From the volumes of the distillate and the composition of the hydrocarbon phase, the new over-all composition in the cell was calculated by the mole balance. The remaining components with the calculated overall compositions were used for the next stage of testing (at the same temperature). This was our new test procedure to examine the

compositional effects on the K-values.

In SWID tests (SWID-1 or SWID-2), after each stage of equilibrium, the overhead samples including hydrocarbon and water vapors were withdrawn from the vapor phase and were condensed. The hydrocarbons were separated from the water and their volumes are measured. The HC sample was collected for chromatography analysis.

Compositional analysis by gas chromatography. Gas chromatographic analysis was conducted in two ways. Heavy oil analysis is generally done using a specially modified simulated distillation technique to accurately account for heavy ends that do not elute during analysis. In this method the chromatograph retention time is calibrated versus *n*-alkane carbon number, and the absolute response on a mass basis is calibrated by comparison with an external standard, a 100% eluted light crude oil. Because the oil mixtures are thick, the oil samples had to be cut with carbon disulfide (CS₂) before introduction into the GC. This latter procedure effectively imposes an addition correction for the CS₂ diluent.

Simple oil characterization. Densities were measured with a DMA 48 densitometer. In cases where the sample size was not sufficient for electronic density measurement, a calibrated μ L syringe was used.

Molecular weights were determined by vapor pressure osmometry (VPO) using tetrahydrofuran solvent, and/or freezing point depression (FPD) using *para*-xylene solvent.

Vapor Pressure Data. Vapor pressure measurements on Kern River fluids were made using an isoteniscope. The standard method used by Phoenix Chemical Labs was ASTM D - 2388.²⁹ The results are related to the phase envelope of the mixture, and are probably close to the bubble point curve of the mixture.

Results and Discussion

In conventional gas/oil reservoirs the reservoir is defined not only by the reservoir matrix but also by the fluids contained within the rock. As the reservoir is produced the reservoir pressure and temperature, and the composition of the fluids change. These changes are studied in phase behavior studies and are necessary for estimating the performance of the reservoir. For heavy oil reservoirs under steamflood some analogous but different behavior is taking place. The injection of steam is placing a gas, water vapor, in the reservoir, and the temperature and pressure of the reservoir are changing. Although there are exceptions, most heavy oil reservoirs prior to steam injection contain water and hydrocarbon in the liquid phase. There is little or no gas cap or vapor space. As the steamflood matures, oil and water are heated, removed from the reservoir and a steamchest forms. In a mature steamflood, like Kern River, steam has broken through to the production wells. At the production well, liquid phase oil and a vapor phase called 'casing blow' are often produced. The 'casing

blow' is composed of water, a light hydrocarbon condensate, and non-condensable gas. The production of hydrocarbon condensate is the clearest evidence that compositional changes are occurring in the steamflood process. To fully access the overall performance of a reservoir under steamflood the pressure, temperature, and hydrocarbon compositional changes need to be accounted for. To include compositional changes in the reservoir model of a steamflood requires generating PVT like properties for heavy oil, a somewhat oxymoronic concept. Traditional PVT studies measure bubble points, etc., to generate EOS parameters for prediction and modeling purposes, but researchers have been loathe to conduct studies using heavy oil and water. For heavy oils under steamflood, other properties may be measured to gain access to PVT type data. In the approach proposed here, oil vapor pressure data are expected to be related to the phase envelope of the oil and the boiling point, and steam distillation data should yield information about water/oil interactions.

The hydrocarbons used in the present study were: water-free Kern River condensate, AWT #6 oil, Station 36 oil. The Kern River condensate and oils were obtained from the field, and where necessary were dewatered by vacuum distillation. The properties of the oils are summarized in Table 1. Station 36 oil is generally accepted as an average produced oil from the Kern River field. Extensive steam distillation experiments were conducted with Station 36 oil. The other fluids are included to get an idea of the vapor-liquid-equilibria (VLE) that may exist for these systems. Vapor pressure measurements were made on the three samples of Table 1. Steam distillation studies including compositional analysis were carried out with Station 36 oil.

Vapor Pressure Measurements. The pressure of the vapor exerted by a crude oil is useful in the development of an equation-of-state, and in making estimates of the gross vapor composition of the steamchest in terms of a vapor phase steam-oil ratio. It is also strategic to the understanding of the steam distillation mechanism. Vapor pressure measurements, although strictly defined for a single component fluid, can be performed on mixtures of components like crude oils.

The vapor pressure was determined on three samples of Kern River fluids. Measurements commenced at room temperature and were continued up to nearly 14.7 psia (Fig. 2). The temperature at which the oil reaches a pressure of 14.696 psia is related to the simple boiling point of the mixture in a one plate boiling apparatus.

At 100 °F the fluids have negligible pressures; condensate has a pressure of 0.04 psia and the two crude oil pressures are < 0.002 psia. At 300 °F the pressures are higher; the condensate pressure is > 3.0 psia and the oil pressures are ~ 0.2 psia. As a consequence, for a steam system temperature of 300 °F, the hydrocarbons may contribute 0.2-3.0 psia to the total system pressure. Saturated steam at 300 °F exerts a pressure of 67 psia. Under ideal gas law conditions, a saturated steam-Kern River hydrocarbon system would be expected to exhibit a total system pressure between 67.2 and 70 psia. Under these same conditions

the estimated steam-hydrocarbon volume ratio in the vapor phase would be in the range of 32-499.

The two Kern River crude oils appear very similar in their vapor pressure-temperature curves, but AWT #6 oil exhibits a slightly lower pressure at each temperature compared to Station 36 oil. This indicates that AWT #6 oil contains a smaller amount of more volatile components, and is consistent with its higher viscosity (Table 1).

The predicted boiling points of the oils from the extrapolation of the temperature-pressure lines to 14.696 psia, shows that condensate will boil at > 400 °F. The boiling points of the oils are > 600 °F. These are boiling estimates for one theoretical plate and do not represent the true boiling point (TBP) of the oils. The results are included for future modeling purposes. EOS and K-value approaches should enable modeling of these results.

Steam Distillation Yields of Kern River Crude Oil. Steam distillation tests yield the amount of oil vaporized by a given amount of steam at certain temperature and pressure conditions. The experiment approaches an equilibrium flash of an oil/water PVT type system, but how close the steam distillation test is to an equilibrium flash is unknown at present. It is currently assumed to be very close. The steam distillation test generally isolates the steam distillation mechanism from all other mechanisms that might be occurring in the steamflood process. Because the distillation mechanism is so isolated by this experiment, the overall results by themselves do not directly relate to a conventional measurable field event, but are related to overall steamflood performance. Specific events within the steam distillation experiment, especially at early steam throughput may provide estimates of composition and water-oil ratio in the vapor phase, useful in certain logging methods of steam zones, and for gross estimates of K-values used for simulation. As more precise instrumental techniques, fluid analyses, and simulation become available, steam distillation results may be better related to the amount and quality of 'casing blow' produced in the steamflood process.

Steam distillation measurement in the laboratory involves passing steam through an oil phase in a fixed volume cell at a certain temperature and pressure. Steam distillation experiments can be conducted under saturated or superheated steam conditions. The steam distillation experiment can be run dynamically (DDT) or stage-wise (SWID). TAMU has developed the stage-wise isochoric (constant volume) distillation (SWID) method and variations. Briefly, in the constant volume SWID procedure oil and pure water are equilibrated at test temperature and pressure conditions. A sample of vapor is then removed and condensed, and the condensed phases are measured and analyzed. The condensed phases consist of water and a light hydrocarbon distillate or overhead. In a modified SWID, after vapor removal, additional water may be injected into the cell to replace the water produced. The sampling cycle is continued after re-equilibration of the water and oil. The

temperature may be held constant throughout the experiment (SWID Type 2) or it can be changed between sampling cycles (SWID Type 1).

In the steam distillation tests the initial Kern River Station 36 oil volume for most tests was 500 cc in a 2000 cc temperature controlled distillation cell. In some cases, water was initially present in the cell and in some cases there was no water initially present. The water injection rate in dynamic steam distillation tests was 1 cc/min (nominal), where applicable. The steam distillation conditions of the dynamic (DDT) and stagewise isochoric distillation (SWID 1 and 2 type) tests conducted with Kern River oil are summarized in Table 2. Complete details of the experimental results have been given elsewhere.²³

Six isothermal steam distillations, which include SWID-2 and DDT types, were conducted using Kern River oil. Two steam distillation runs were completed at 300 °F (Runs B07 and B08) and two distillation were completed at 400 °F (Runs B09 and B10). One run (B02) was conducted at 467 °F, and one run (BBR3) was completed at 500 °F.

Four variable temperature steam distillations, SWID-1 type, were completed with Kern River oil. Runs B04, B05, and B12 were initiated at 300 °F, and the temperature was increased after each overhead withdrawal. In most cases water was initially in contact with the oil. One other variable temperature run (SWID 1), B13, commenced at 400 °F.

The amounts of oil produced (steam distillation yield) at the final steam throughput (steam factor) are summarized in Table 3 for each of the steam distillation runs with Kern River oil. Kern River Station 36 oil was distillable under all test conditions. The maximum oil yield due to steam was $>15\%$ in a 400 °F isothermal steam distillation run (B09) with a 3.543 steam factor. The 300 °F runs, B07 and B08, had lower yields. Variable temperature (SWID-1) runs show appreciable yields at lower steam throughput.

The oil production curves for steam distillation experiments conducted at 300 °F (Fig. 3a) show a steam distillation yield as high as 10% of the initial oil at a steam distillation factor of 4.599. The two runs, conducted with slightly different experimental procedures, have different yield curves. The only similarity is in the production at the beginning of the steam distillation, after that, the curves diverge. Run B07 was conducted in modified dynamic mode (*m*SWID-2) with water injected in a batch-wise mode after each depletion. Run B08 was conducted as a dynamic distillation with water injection and vapor production occurring continuously. The differences in yields appear to be a function of this process. The higher production curve and overall yield of the dynamic test (B08) may be the result of more efficient mixing and equilibration of water/oil/steam.

Process effects are presented by examining the difference in yield profile of *m*SWID-2 (B07) as compared to the dynamic Run B08. Both processes were performed at 300 °F, but the means of injection and production was varied. The *m*SWID-2 injection and production were done in a batch manner. This test was performed at a condition expected to be closer to

equilibrium than the conditions of Run B08. It appears that the continuous steam injection of the dynamic distillation process may provide more agitation and greater steam/oil contact than the batch method. The dynamic steam yields are higher, compared to the expected near equilibrium process of *m*SWID-2. This may be due to increased steam hydrocarbon contact area and mass transfer, i.e. enhanced hydrocarbon vaporization.

The yield data at 400 °F (Fig. 3b) show a steam distillation yield of at least 14% at a steam distillation factor of 3.800. The two runs have significantly different yield curves. Run B09 had no water in contact with the oil at the start of the distillation.

The average cell pressure during this distillation run was 100 psia (Table 2). Because of this initial condition and the 400 °F cell temperature, the steam distillation proceeded under super heated steam conditions. The B10 distillation run was at the same temperature but with water initially present. This condition created saturated steam conditions evidenced by the higher cell pressure, 250 psia. In this particular case, superheated steam distilled ~25% more oil than saturated steam at an equivalent steam (CWE) throughput. The lower yield in the presence of initial water and at higher pressure is suggestive of the suppression of hydrocarbon vaporization due to the water. When water is not present, the hydrocarbon vaporization can proceed more efficiently. The presence of water apparently inhibits the mass transfer rate or the rate of vaporization of the light hydrocarbon components from the liquid phase to the gas phase.

The results of the dynamic distillation tests and one modified dynamic test for Kern River oil are summarized in Fig. 4. This figure plotted in a logarithmic scale for V_w/V_{oi} represents all the experimental effects that have been observed in the current steam distillation studies of Kern River oil. The effects include the trend of distillation yield with distillation factor, temperature dependence, process effects, and distillation pressure or steam saturation influence.

The trend of distillation yield with distillation factor on a logarithmic scale is clearly increasing for all of the steam distillation tests conducted for Kern River at steam throughput factors up to 8.0. This increase is not asymptotic as it was assumed previously. Linear plots of steam distillation results misled early workers into suggesting that the distillation yield for a given oil was nearly constant above a certain volume of steam injection and independent of temperature.¹² The logarithmic plot also shows a temperature effect of increasing distillation at higher temperatures, and a distillation yield that increases with steam throughput. The results are not inconsistent with the eventual steam distillation of all of the oil at unlimited steam throughput. Although this is not practical, it does suggest that the residual oil near an injection well in a mature steamflood may show much greater distillability and light end losses than expected from laboratory tests.

Temperature dependence is presented by comparison of dynamic distillation tests (DDT) B08, B09 and B02. The hydrocarbon yield increases as the steam temperature is raised.

The 'Magic' of Steam. The action of steam on oil has two very important effects. One of them has been exploited for oil recovery by steam injection; the other one has largely been neglected or included in an oblique way. Steam provides heat to the oil in a reservoir. This heat reduces the viscosity of the liquid oil and facilitates movement of the oil to the producing well. Steam also creates a vapor or gas space in the reservoir into which oil can distill or vaporize. This later effect is the 'magic' of steam for the sake of this discussion. The vaporization of some of the oil into the gas phase and subsequent movement with the steam and possible condensation and re-vaporization mechanisms have not been extensively exploited in steamflood operations.³⁰ The distillation mechanism has important application in the overall steamflood process and may have a wider application in downstream operations. The 'magic' of steam is really based on the combination of Dalton's Law of partial pressures and Raoult's Law of partial pressures and liquid phase compositions as applied to water/oil/vapor systems.³¹ The vaporization mechanism maybe subliminally included in previous steamflood evaluations through the adjustment of relative permeability curves and recovery endpoints.

Some of the 'magic' of steam and its action on Kern River oil can be shown in the results of the steam distillation tests compared to simple distillation (Fig. 5). Steam is able to distill oil components at much lower temperatures than by heat alone. The ancients used this property of steam to separate and concentrate perfume essences from oils. The current steam distillation work allows a comparison between simple distillation and steam distillation to be made, once a basis for comparison is established. The TBP (Total Boiling Point) curve for Kern River Station 36¹⁷ is compared to steam distillation yields at 300 and 400 °F in Fig. 5. The volume of oil vaporized and produced by steam is taken at steam factors of ~4.0 for the 300 and 400°F dynamic steam distillations. This comparison is specific to the water throughput (steam factor) of the steam distillation runs, which was ~4. The ASTM D-2892 results show that Kern River oil does not distill below 400 °F using heat only. Yet steam at 300 °F and a steam factor of ~4 distills about 10% of the oil. This effect is what is referred to above as the 'magic' of steam, and is a key mechanism in steamflood recovery.

Vapor Phase Steam-Oil Ratio Estimates. The steam-oil ratio in a laboratory test is an indicator of how much hydrocarbon is present in the steam chest of a mature steamflood. The steam-oil ratio in the vapor phase (VSOR) can be easily calculated from laboratory steam distillation production data, and is a coarse independent check on the vapor pressure data. Such data may be useful in the calibration and corrections of some logging tools that respond to both water and hydrocarbon, like a Carbon-Oxygen log.

The steam-oil ratio (VSOR) is the ratio of the volume of steam to the volume of the oil in the vapor state at the temperature and pressure conditions of the distillation. Each overhead produced in the steam distillation test represents the

volume ratio of the vapor phase in the distillation cell. The VSOR in the steam distillation experiment is merely the ratio of the steam factor (V_w/V_{oi}) to the steam yield (V_o/V_{oi}). This information is useful in estimating the gross water and hydrocarbon composition of the vapor phase in the steam chest of an actual steamflood.

For steam distillation runs using Kern River oil at 300 and 400°F the VSOR with steam throughput are summarized in Fig. 6. The ratio increases with steam injection. The ratio at early production represents a lower limit of the VSOR value. The VSOR based on the first steam distillation overheads appear to be temperature dependent, and vary from an average of 256 in the 300 °F runs to 97 in the 400 °F runs. The value of 256 at 300 °F is in the middle of the estimated range of 32-499 based on vapor pressure arguments above. The ratio on a mass basis is calculated by correcting the volume ratio for the appropriate densities and is also included in Fig. 6. On a mass basis the initial ratio is an average of 26 at 300 °F and 10 at 400 °F.

The results give an order of magnitude estimate of how much hydrocarbon could be in the vapor phase in a steamflood. The amount is not significant to a reserve estimate, but may affect logging tools that respond to oxygen and carbon densities.

Compositional Changes During Steam Distillation.

Compositional analyses of the overheads from the steam distillation runs were conducted at EPTD using modified simulated distillation procedures to obtain the hydrocarbon distribution in terms of an equivalent alkane carbon number. The gas chromatography procedures have been described elsewhere.¹

Steam distillation vaporizes light ends in the composition of even heavy oils at all temperatures investigated in this study, 300 - 500 °F. The steam vaporization process is not constant (Fig. 7), and steam continues to vaporize or distill heavier and heavier hydrocarbons. The compositional distributions of the overheads from the steam distillation Run B07 at 300 °F (Fig. 7), show large changes from the first overhead to the last sample. The distribution of B07-1 distillate peaks at a carbon number of 12 while the last sample at high steam throughput peaks at carbon number 15. The effect of steam throughput on the overhead distribution is significant even for steam experiments at 300 °F. The boiling temperature of C_{12} is near 420 °F while C_{15} boils at ~510 °F. Thus 300 °F steam is vaporizing hydrocarbon components in the oil that have boiling points well above the steam injection temperature.

Similar results were obtained in Run B08 at 300 °F. This run differs from B07 in that it was carried out to higher steam throughput. The overhead distributions change even more dramatically with additional steam throughput (Fig. 8). The compositions were sampled on every other distillate. The sample numbers are roughly spaced according to steam throughput up to a V_w/V_{oi} of 4.6 for sample B08-15. The maximum in the hydrocarbon distribution of the overhead changes from 12 in the first overhead to 17 in the last overhead at a steam distillation factor of 4.5. The effect of steam

throughput on the overhead distribution is more dramatic when looking at the tails of the distributions at high carbon numbers. When the sensitivity of the scale is enhanced, it is clear that steam at 300 °F is distilling measurable hydrocarbons through at least carbon number 26.. 8.6% of the composition on a mass basis occurs above a boiling temperature of 620 °F for the last distillate (B08-15). A carbon number 26 normal alkane has a boiling point of ~750 °F. Thus 300 °F steam has the energy to distill heavy hydrocarbons that boil at temperatures much higher than 300 °F. This is consistent with the suggestion above that steam may vaporize all of the oil at an infinite steam throughput. Steam distillations of Kern River Station 36 oil at 400 °F show similar behavior, but additional hydrocarbon production. In Run B09 the oil was distilled with super heated steam. The compositional distributions of the overheads from the 400 °F super heated steam distillation (B09) run, show a large shift to heavier hydrocarbons at increased steam throughput. The hydrocarbon distribution at early production peaks at C_{13} . Midway through the steam injection the maximum in the hydrocarbon distribution has shifted to C_{15} , and the last production peaks at C_{17} . Steam distillation overhead distributions at 400 °F under saturated steam conditions were similar to the super heated case. The yield is lower in the saturated steam case (Run B10), but the overall distributions are similar. At early production, the peak in the hydrocarbon distribution is C_{13} , at mid production it is C_{15} , and at longer steam throughput the peak shifts to C_{17} .

In steam distillation Run B12 the temperature was varied from 300 to 500 °F. The composition of the initial overhead (B12-1) has a peak at carbon number 11, and the last production, at a steam temperature of 500 °F, has a peak at carbon 14. The variable temperature studies give a broad look at steam distillation over changing conditions of steam throughput and temperature. However, so many conditions are changing simultaneously that specific field related information is not as useful as isothermal experiments. The variable temperature distillation may represent near injection well phenomena at the beginning of the steamflood. One constant temperature (SWID-2) steam distillation was conducted at 500 °F under saturated steam conditions (Run BBR3 conducted at 699 psia). This steam distillation was conducted at very low steam throughputs, up to a throughput of 0.3. The yield is not comparable to the other isothermal floods at higher throughputs. The composition of the distillates at these low throughputs look similar. The hydrocarbon distributions peak at C_{13} for all the samples. However, the surprising result appears in the tail of the compositional distributions of Kern River distillates at this 500 °F condition.

The magnified distributions of the distillate tails show significant population of C_{21} - C_{30} hydrocarbons at low steam throughput. This covers hydrocarbons with boiling points in the range of 640 - 840 °F! Thus a 500 °F steam distillation is capable of vaporizing oil components with boiling points in the 600 - 800 °F (C_{20} - C_{30} +) range. For the last overhead collected in this run, 15% of the mass distribution occurs above a boiling

point of 640 °F. This has important implications in the thermal models used in numerical simulation of steamfloods designed for higher temperatures than Kern River. Current trends toward few pseudo components and non-volatile heavy ends may not be adequate to describe the compositional behaviors observed here. It is very clear based on compositional analyses that steam distillation vaporizes heavier and heavier hydrocarbons as the distillation process proceeds. This phenomenon can be verified in other physical properties of the overheads including density, viscosity, and molecular weight.

Distillate Density Changes During Steam Distillation. The density and viscosity of produced steam distillates were measured where there was sufficient sample. Density is a required measurement for compositional analysis, but because of the small quantity of some samples an alternate method of density analysis using an calibrated syringe was developed for very small samples. The results of both methods are included here for comparison. Viscosity measurements, which usually require at least 2 ml of sample, were measured where possible, and are discussed below.

The densities of produced samples from the steam distillation of Kern River Station 36 oil at 300 °F show an increase with the amount of steam throughput (Table 4, Fig. 9). This is consistent with the loss of light ends at early times of the distillation and vaporization of heavier ends as the steam distillation proceeds. The densities and viscosities of produced samples from the steam distillation of Kern River Station 36 oil at 400 °F under superheated conditions show a higher increase in density with the amount of steam throughput (Table 4, Fig. 9). This is consistent with the generalized vaporization mechanism discussed above, and with the suppression of vaporization due to the presence of water. The densities of the overheads also go to higher values compared to the distillation at 300 °F. The densities and viscosities of produced samples from the steam distillation of Kern River Station 36 oil at 400 °F under saturated steam conditions show an higher increase in density with the amount of steam throughput (Table 4, Fig. 9). This is consistent with the generalized vaporization mechanism. The densities of produced samples from the variable temperature steam distillation of Kern River oil (SWID-1) also show the trend of increasing density with the amount of steam throughput (Table 4, Fig. 9).

Rheology of Steam Distillation Effluents. Rheological data on the steam distillation overheads would be useful for tuning computational models of the steam distillation process. The cell size, charge volumes, and experimental procedures used in the experimental setup permitted the collection of sufficient overhead volumes for viscosity measurements.

Viscosities at three temperatures were measured for distilled hydrocarbon samples from the 300 °F steam distillation Run B07. Ambient temperature viscosities versus steam throughput were measured for overheads from 400 °F superheated and saturated steam distillations, Runs B09 and B10 respectively.

The results in this section represent the most comprehensive rheological measurements on steam distillation samples from one oil, Kern River oil, under a number of steam distillation conditions. Some ambient temperature viscosity data for steam distillation overheads has been included in Table 4, and viscosities with temperature are summarized in Table 5.

The general trend of produced distillate viscosity with steam throughput is increasing (Fig. 10). Viscosities of produced distillate samples from the 300 °F steam distillation are included in Fig. 11. To obtain sufficient sample for the viscosity with temperature measurements, the first 8 produced samples were combined into two samples. Overhead samples 0, 1, 2, and 3 were combined as were samples 4, 5, 6, 7, and 8. Large viscosity changes are to be noted in a comparison of the early distillate sample (B07 0-3) to the late distillate sample (B07 4-8). The viscosity increases by nearly a factor of two, from 3.52 cp to 6.02 cp, at 77°F as the steam distillation proceeded. This observation of increasing viscosity with steam throughput in a steam distillation experiment was suggestive of a possible method to estimate a steamflood life by analysis of the hydrocarbon condensate or 'casing blow'. For comparison, the viscosity with temperature results for Kern River condensate are included in Table 5. Based on the absolute viscosity values and the temperature dependence the Kern River condensate appears similar to the production sample at low values of steam throughput. This similarity to early steam distillation samples is also reflected in the density data. In one approach, Kern River has been steamflooded for 20 years, and the condensate would be expected to change. However, it appears to be similar to the first overheads from a steam distillation experiment. It appears that the produced condensate from the field is not directly indicative of the overhead at large steam throughput from a steam distillation experiment. 'Casing blow' condensate produced in the field represents a relatively light hydrocarbon fraction from the overall Kern River oil that does not condense in the steamflood. It may represent only a fraction of the hydrocarbon vaporized in the steamflood process.

The viscosities of produced distillates from 400 °F steam distillations show similar trends and are summarized in Fig. 11.

Molecular Weight Changes During Steam Distillation. Molecular weight determinations of condensed steam distillation overheads were measured where possible to corroborate results from compositional, viscosity, and density measurements, and to extend the available information on the character of steam distillation overheads of Kern River oil. The results of molecular weight measurements by freezing point depression (FPD) taken on all the available Kern River Station 36 steam distillation samples are given in Table 6. Samples from steam distillations at 300 °F were not measured. The results are summarized according to sample number, related to steam throughput, to facilitate tabulation. Sample numbers are cross-referenced to steam factors for Runs B09, B10, and B04 in Table 6.

The first set of constant temperature results are B09 and

B10, steam distillations at 400 °F. As observed in the other physical properties of viscosity and density, the molecular weight of the produced samples generally increased with steam throughput (Fig. 12). Fluctuations appear in some sample series. This is attributed to changes and adjustments in the backpressure. The molecular weights of the overheads for the superheated steam distillation (B09) appear higher, with the molecular weight getting as high as 290. The saturated steam case (B10, Fig. 12), does not show a trend to as high molecular weights as the superheated case. This is consistent with the presence of water in the saturated steam casing suppression of the vaporization of hydrocarbon. Analysis of overheads from steam distillation Runs B04 and B12 form a second set of variable temperature (SWID-1) results (Fig. 12). The trends with steam throughput are the same. The molecular weight of the produced hydrocarbon samples increased with steam throughput.

Molecular weights may also be estimated from GC compositional distributions. No FPD data were measured for distillates from the 300 °F steam distillations, Runs B07 and B08. However, based on the GC hydrocarbon distributions of the produced samples molecular weights were obtained using the equivalent alkane approximation (Table 6).

Comparison of Kern River Condensate And Distillates.

Initially, laboratory steam distillation studies were expected to bear on the age of a field steamflood. Analysis of the overhead compositions with steam throughput in laboratory steam distillation tests and comparison to produced 'casing blow' condensate from the reservoir was expected to be related. Such information could aid in the evaluation of steamflood performance and mechanism. However, Kern River 'casing blow' composition and produced amount do not appear directly related to current or past laboratory steam distillation tests. Kern River 'casing blow' does seem similar to early yields in laboratory steam distillation tests. The implications will be discussed in this section.

Steam distillation studies in the minimum provide a valuable demonstration of the origin of 'casing blow' condensate in conventional steamflood operations. The composition of the distillates also reveals an important part of the energy mechanism at work in steamflooding. The heat energy not only lowers the viscosity of the oil but also vaporizes hydrocarbons. Laboratory studies show the composition of the distillates increases to higher carbon numbers with the steam temperature and with steam throughput. All of these effects are expected to occur in the field and should be in thermal numerical models.

Some condensate properties were discussed earlier. Data are gathered here for a better comparison of 'casing blow' and steam distillation properties. The physical properties of density (ρ), molecular weight, viscosity (μ), and composition of Kern River 'casing blow' are compared to the first distillates produced in 300 and 400 °F steam distillations of Kern River crude oil in Table 7 and Fig. 13.

The Kern River steamflood runs at an average temperature of 240°F in the steamchest mid-point between the injector and

producer. Steam is probably injected at near 400 °F. The amount of 'casing blow' produced relative to oil has an historical high around 3% and has diminished to ~0.6% before a 'casing blow' shut-in program began. The 'casing blow' physical properties appear similar to the first overhead in the 300 °F laboratory steam distillation. The first overheads were obtained at low steam throughputs. Kern River steamflood is at least 20 years old, and dominated by gravity forces. Yet the condensate has physical properties similar to early production in a laboratory steam distillation.

The hydrocarbon composition of condensate (Fig. 13) is also similar to the early steam distillation production in the 300°F distillation. These results bring up and imply important differences between the laboratory distillation process and the field performance, which includes the mixing of distillates and crude oil.

The one parameter that could unite all these observations and result is the casing system temperature. The casing system temperature appears to be the most important parameter in determining the quality and quantity of 'casing blow' in a steamflood. At Kern River producing well bottom hole temperatures may be in a range of 212-225 °F. No laboratory steam distillation has been conducted in this temperature range. However, the effect of temperature on steam distillation observed in this report suggest that the hydrocarbon casing production will be much lower and consist of lighter components in the field compared to laboratory studies at 300 - 400° F. The corroboration of this hypothesis awaits future laboratory and/or simulation work.

Conclusions

- * Steam distillation causes large compositional changes in Kern River oil. The oil produced by steam vaporization is not like the original oil. Vaporized oil was 20 gravity units lighter than Kern River Station 36 oil. Viscosity, molecular weight, and composition were also changed.
- * The steam yield of Kern River oil in laboratory studies under saturated injection and withdrawal conditions is affected by three factors: 1) the temperature of the steam, 2) the amount of steam, and 3) the steam distillation setup. The amount of vaporized oil produced by steam distillation increased with steam temperature and steam throughput. The increased yield with amount of steam implies that the steam distillation process may still be an important mechanism in the steamchest of a mature steamflood.
- * Hydrocarbon condensate ('casing blow') produced in the mature Kern River steamflood is similar to distillates produced at low steam throughput in laboratory steam distillation studies. This observation along with other results on the effect of temperature implies that the most important controlling field parameter for 'casing blow' composition and amount is the temperature within the casing system.
- * Additional core studies are recommended that focus on the application of laboratory and/or simulation techniques to predict field 'casing blow' quality and quantity at producing

well conditions.

- * The vapor phase steam oil ratio on a mass basis could be as low as 10-20 based on laboratory steam distillations. The presence of some hydrocarbon in the steam may affect logging tools that respond to oxygen and carbon densities.
- * Superheated steam vaporizes more oil than saturated steam. In comparative runs at 400 °F superheated steam distilled 25% more Kern River oil than saturated steam. This interesting effect noted in previous work probably has little application in the field where superheated steam conditions are unlikely, but could be useful in a surface upgrading technique.

Nomenclature

AWT= automatic well test site

DDT= dynamic distillation test

EACN= equivalent alkane carbon number

FPD= freezing point depression

HC= hydrocarbon

IDA= isochoric distillation analysis

MBM= material balance model

μ = viscosity, cp

ρ = density, g/cc

SPT= static system pressure test

SWID= stage-wise isochoric distillation test

TBP= total boiling point

VL= vapor liquid equilibrium

VLL= vapor liquid equilibrium

V_o/V_{oi} = steam distillation yield of oil

VPO= vapor phase osmometry

VSOR= vapor steam oil ratio

V_w/V_{oi} = steam distillation factor

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TABLE 1
Summary of Kern River Fluid Properties

Sample	Source	Density, g/cc ^a	Gravity, °API	Molecular Weight	Viscosity, cp ^a
KR Station 36	KR Field	0.9710	13.0	458	10,000
KR AWT #6	KR Field	0.9819	12.6	512	17,000
Condensate	KR Field	0.8700	33.0	190	3.5

^a Measurements at room temperature (75 °F)

TABLE 2
Summary of Steam Distillation Run Conditions

Run ID	Type ^a	Temp Condition	T _{avg} , °F	P _{avg} , psia	V _{wi} , cc ^b	V _{oi} , cc ^c
B02	DDT	Constant	467	500	200	150
B07	mSWID-2	Constant	300	66.7	500	500
B08	DDT	Constant	300	72.7	500	500
B09	DDT	Constant	400	100	0	500
B10	DDT	Constant	400	250	500	500
B04	mSWID-1	Ramped	300-500 ^d	- ^d	500	500
B05	mSWID-1	Ramped	300-500 ^d	- ^d	500	500
B12	SWID-1	Ramped	300-500 ^d	- ^d	500	500
B13	SWID-1	Ramped	400-500 ^d	- ^d	500	500
BBR#3	SWID-2	Constant	500	699	500	500

^a Designations: DDT = dynamic distillation test, SWID-1 = stagewise isochoric distillation at ramped temperature, SWID-2 = stage isochoric distillation at constant temperature, mSWID-1 = stagewise isochoric distillation with ramped temperature and injection of water, mSWID-2 = modified stagewise isochoric distillation at constant temperature and injection of water.

^b Initial volume of water in the cell. ^c Initial volume of oil in the cell. ^d In steam distillation runs where the temperature is ramped, the average temperature and pressure of the runs are process dependent.

TABLE 3
Summary Results for Steam Distillation Runs

Run ID	Steam Distillation Factor V _w /V _{oi}	Steam Distillation Yield V _o /V _{oi}
B07	3.481	0.063
B08	4.599	0.108
B09	3.543	0.155
B10	3.800	0.141
B04	0.803	0.086
B05	1.995	0.110
B12	0.578	0.027
BBR#3	0.312	0.034

TABLE 4

Density and Viscosity Measurements of 300° and 400°F Steam Distillation Overheads

Run	Vw/Voi	Sample #	ρ , g/cc ^a	ρ , g/cc ^b	°API	μ , cp ^c
B07		1-4				3.52
		5-9				6.02
B08	0.822	1-4	0.8626	0.86	31.5	3.1
	2.199	5-9	0.8773	0.876	28.8	5.12
	4.599	10-15	0.8862	0.888	27.0	7.79
B09	0.2	1	0.8588	0.856	32.4	
	0.4	2	0.8707	0.868	30.2	
	0.6	3	0.8779	0.876	28.9	
	0.8	4	0.8832	0.884	27.6	5.12
	1	5	— ^d	0.888	26.8	5.63
	1.3	6	0.892	0.892	26.1	6.66
	1.6	7	0.8967	0.896	25.3	7.68
	1.883	8	0.8993	0.9	24.8	7.17
	2.183	9	0.9024	0.9	24.5	10.24
	2.483	10	0.9047	0.904	24.0	12.29
	2.783	11	0.9074	0.908	23.4	11.26
	3.083	12	0.9093	0.908	23.2	13.06
	3.543	13	0.9117	0.912	22.7	15.36
B10	0.2	1	0.862	0.86	31.7	
	0.4	2	0.8615	0.868	31.0	
	0.6	3	0.8743	0.872	29.5	
	1	4	0.8817	0.88	28.1	
	1.4	5	— ^d	— ^d		
	1.8	6	0.8884	0.888	26.8	
	2.2	7	0.8953	0.896	25.5	
	2.6	8	0.8964	0.896	25.4	8.7
	3	9	0.899	0.9	24.8	10.24
	3.4	10	— ^d	0.9	24.7	
	3.8	11	0.905	0.904	23.9	11.26
B04	0.102	1	— ^c	— ^c		
	0.202	2	0.8657	0.864	32.3	
	0.302	3	— ^c	0.876	30.0	
	0.402	4	0.8837	0.884	28.6	
	0.602	5	0.8955	0.896	26.4	
	0.803	6	0.896	0.896	26.4	

^aMeasured using Mettler DMA 45 density meter. ^bMeasured using syringe technique. ^cViscosity at 75 °F.

^dInsufficient sample.

TABLE 5
Viscosity of 300 °F Steam Distillation Overheads from 300°F Run B07 and Comparison to Kern River Condensate

Temp °C	Temp °F	Viscosity in Centipoise		
		B07 0-3	B07 4-8	KR Condensate
25	77	3.52	6.02	3.44
48.9	120	1.85	3.47	1.89
60	140	1.57	2.62	1.38
71.1	160	1.36	2.11	1.12

TABLE 6
Molecular Weights of Overheads from Steam Distillation Runs

Distillate #	300 °F B07 ^a	300 °F B08 ^a	400 °F B09	400 °F B10	300-500 °F B04	300-500 °F B12	400-500 °F B13
1	<i>-^b</i>	<i>177</i>	210	210	<i>-^b</i>	162	<i>-^c</i>
2	<i>181</i>	<i>-^c</i>	218	206	232	174	<i>-^c</i>
3	<i>195</i>	<i>194</i>	233	218	248	167	<i>-^c</i>
4	<i>204</i>	<i>-^c</i>	231	223	255	175	185
5	<i>219</i>	<i>207</i>	<i>-^b</i>	<i>-^b</i>	269	192	189
6	<i>224</i>	<i>-^c</i>	257	237	266	196	202
7	<i>-^b</i>	<i>216</i>	244	239	261	216	208
8	<i>230</i>	<i>-^c</i>	251	253			
9	<i>230</i>	<i>221</i>	<i>-^b</i>	268			
10		<i>-^c</i>	262	241			
11		<i>225</i>	258	246			
12		<i>-^c</i>	291	279			
13		<i>231</i>	286	271			
14		<i>-^c</i>	277	247			
15		<i>236</i>					
Resid		<i>523</i>					

^a Values in italics were estimated from gc compositional data, all other values were measured by FPD and/or VPO.

^bInsufficient sample. ^cNot measured.

TABLE 7**Comparison of Kern River 'Casing Blow' and Steam Distillate Properties**

Property	Condensate	300 °F B07	300 °F B08	400 °F B09	400 °F B10
ρ , g/cc	0.870	0.87	0.86	0.856	0.86
Mol Wt	190	181	177	210	210
μ , cp	3.44	3.52		5.12	

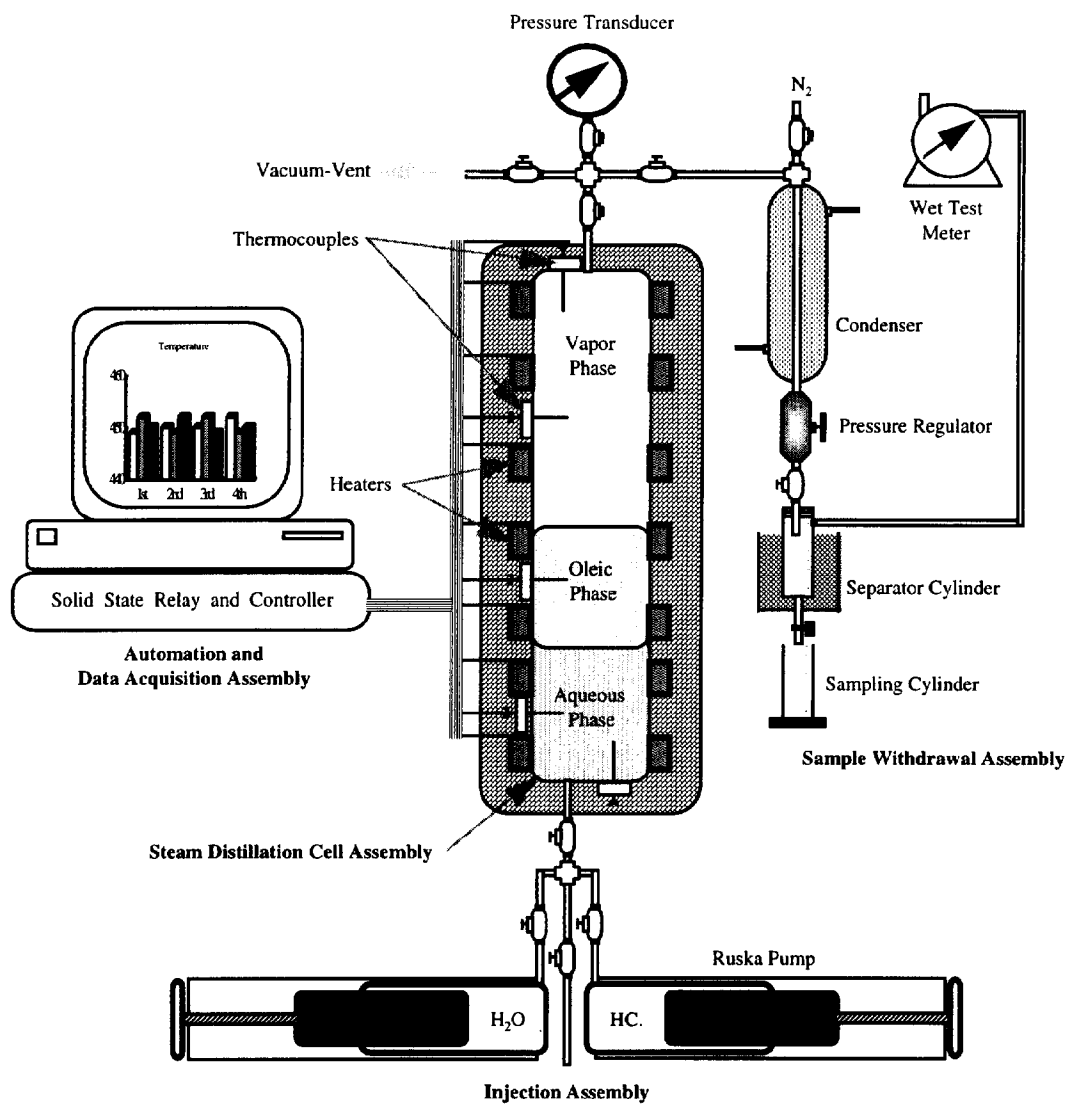


Fig. 1—Distillation Test Apparatus.

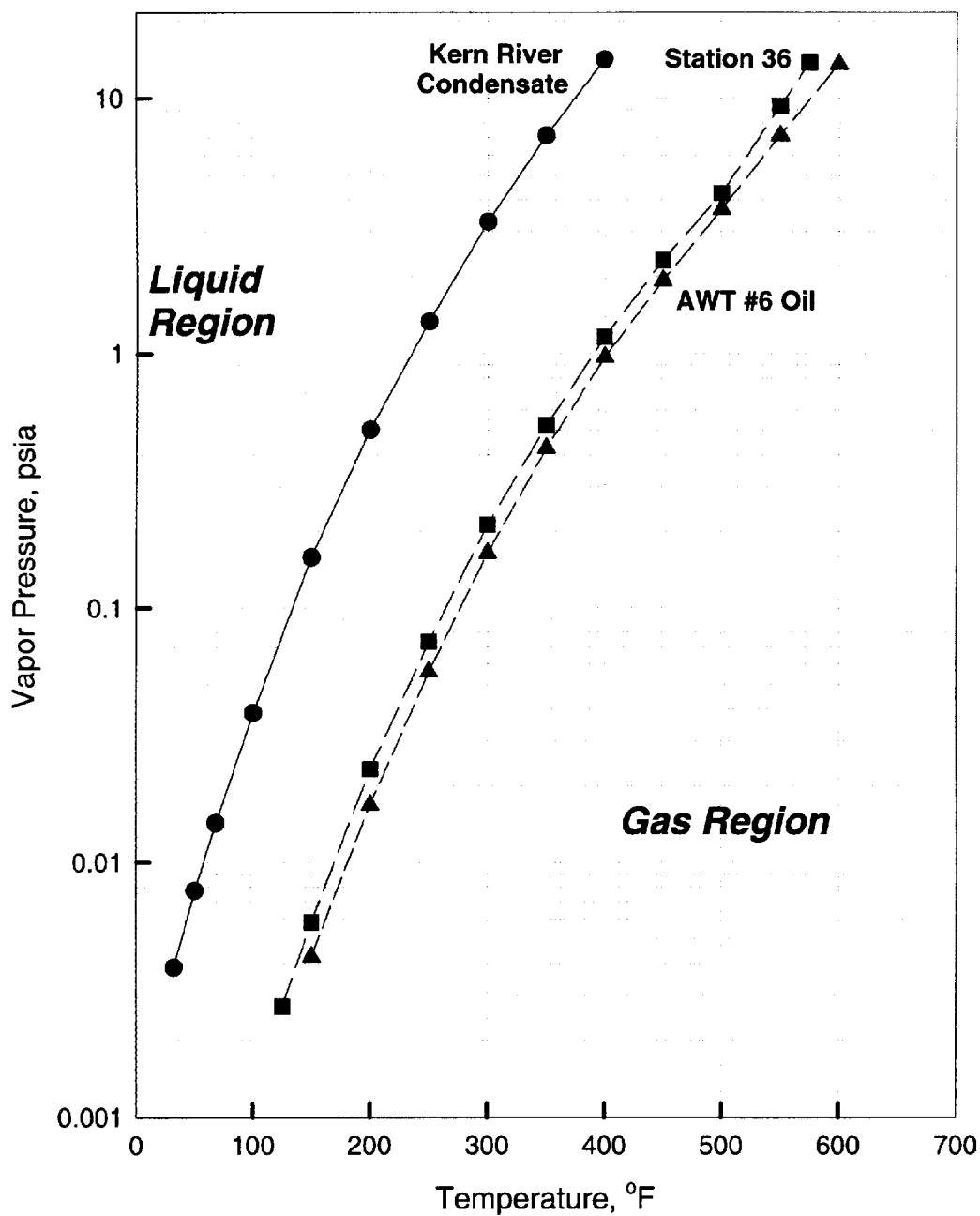
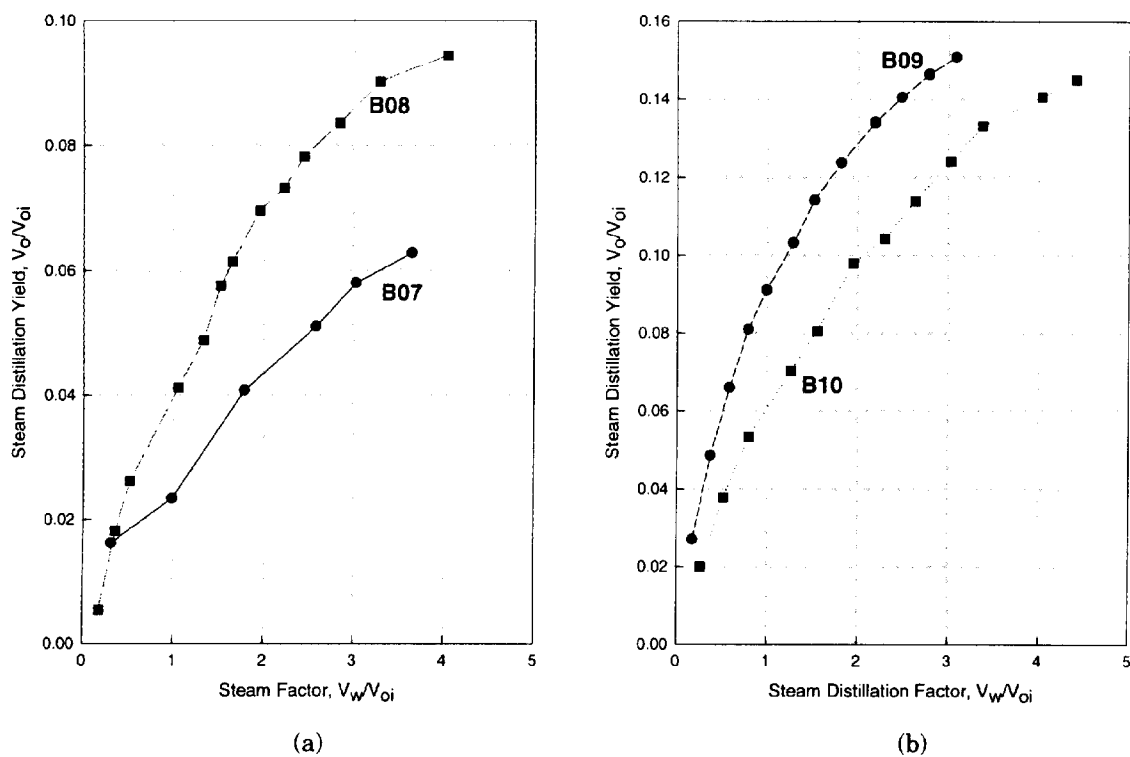


Fig. 2—Vapor pressure measurements by ASTM 2388 for Kern River fluids.



(a) (b)
Fig. 3--Steam distillation yield curves for Kern River oil at (a) 300 °F and (b) 400 °F.

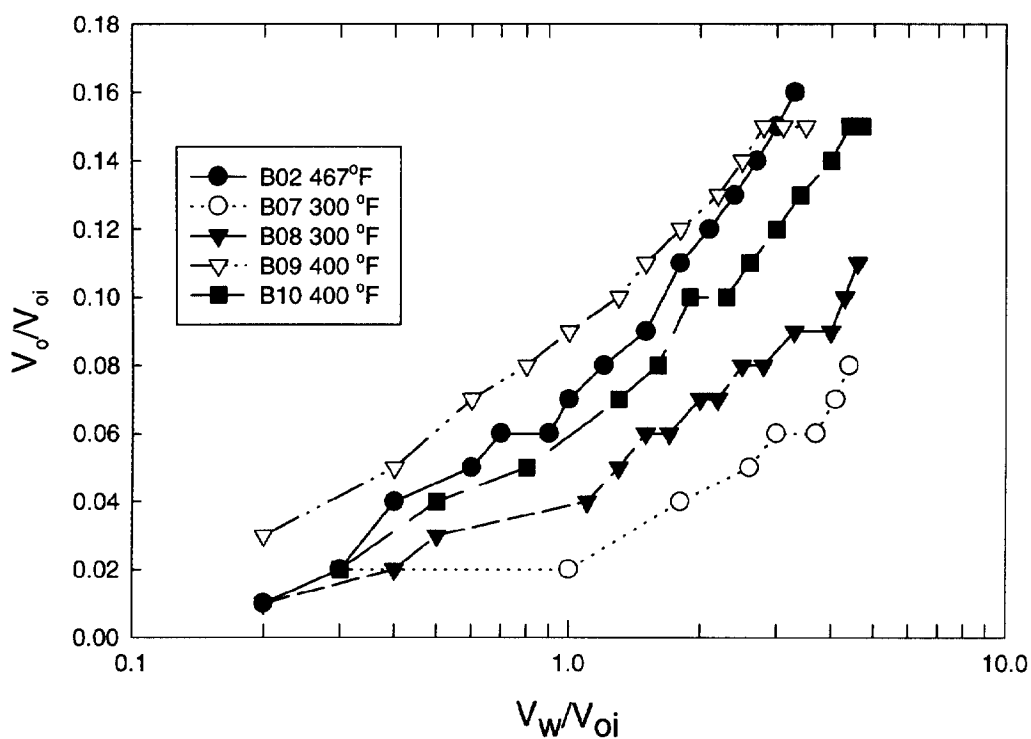


Fig. 4—Steam distillation yields for Kern River crude oil at different saturated steam temperature and process conditions.

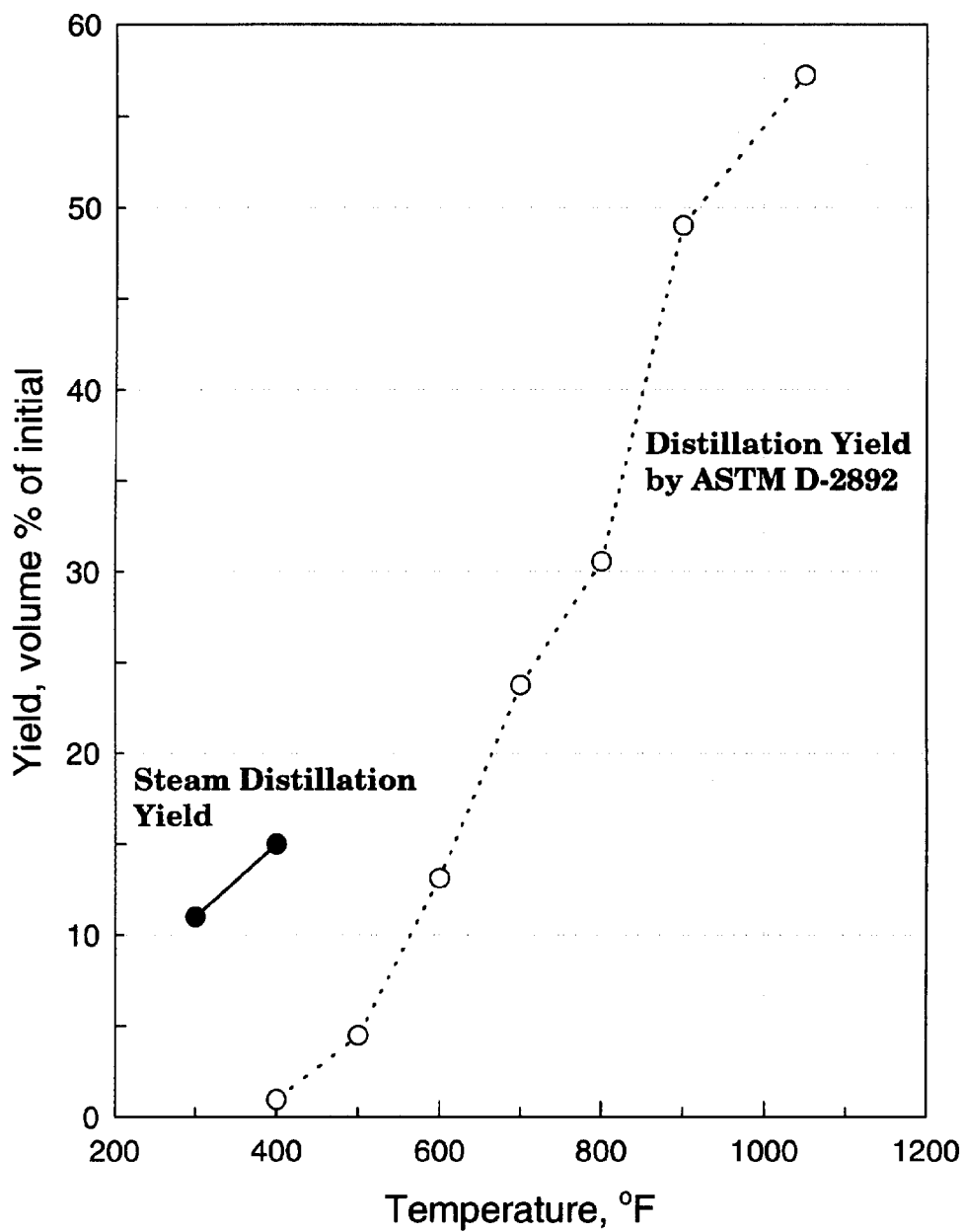


Fig. 5--Yields of Kern River Station 36 by Distillation (ASTM D-2892) and Steam Distillation.

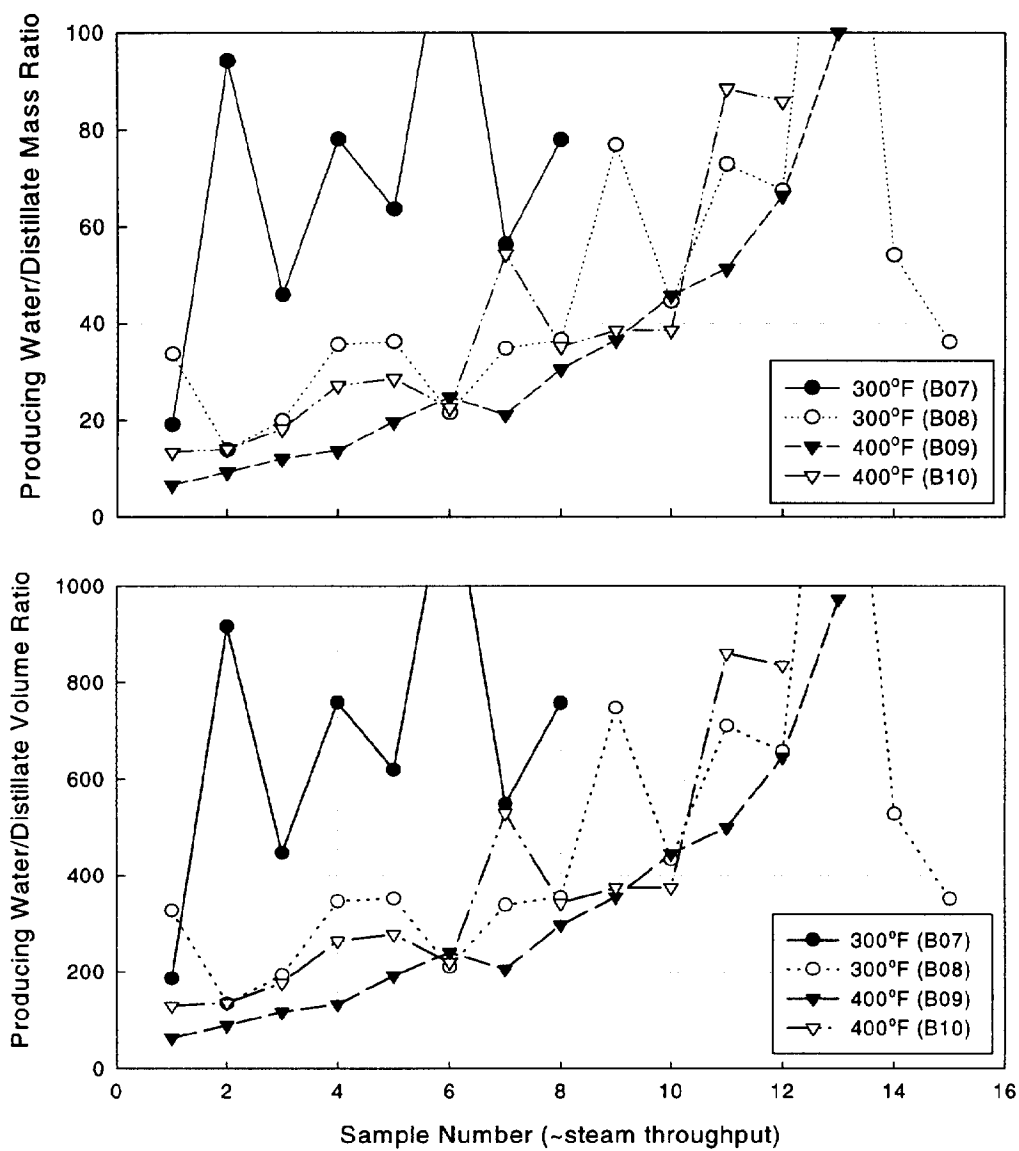


Fig. 6--Vapor phase steam-condensate ratio in mass and volume units from steam distillation of Kern River oil at 300 and 400°F.

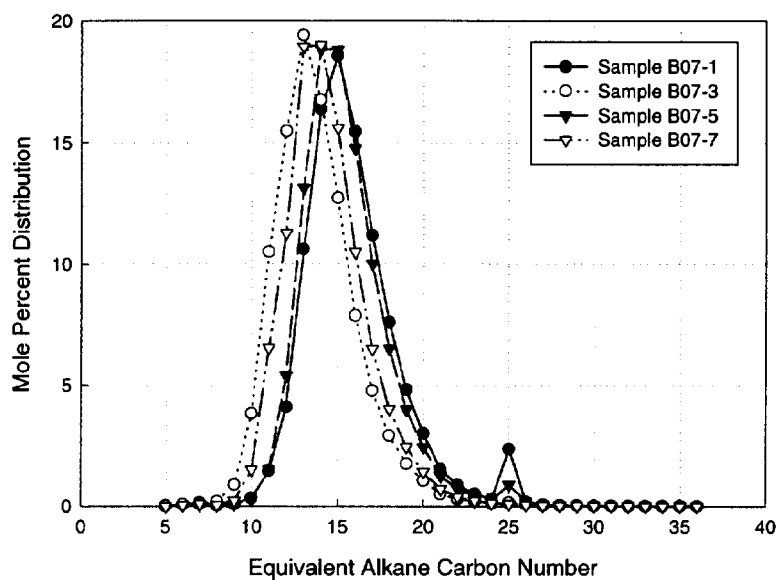


Fig. 7—Compositional distributions of overheads from steam distillation (B07) of Kern River Station 36 oil at 300 °F.

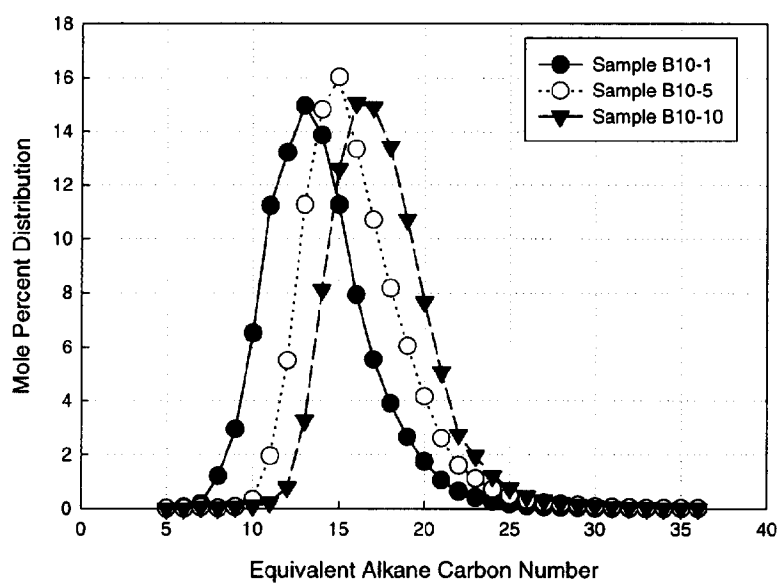


FIG. 8—Compositional distributions of overheads from steam distillation (B10) of Kern River Station 36 oil at 400 °F.

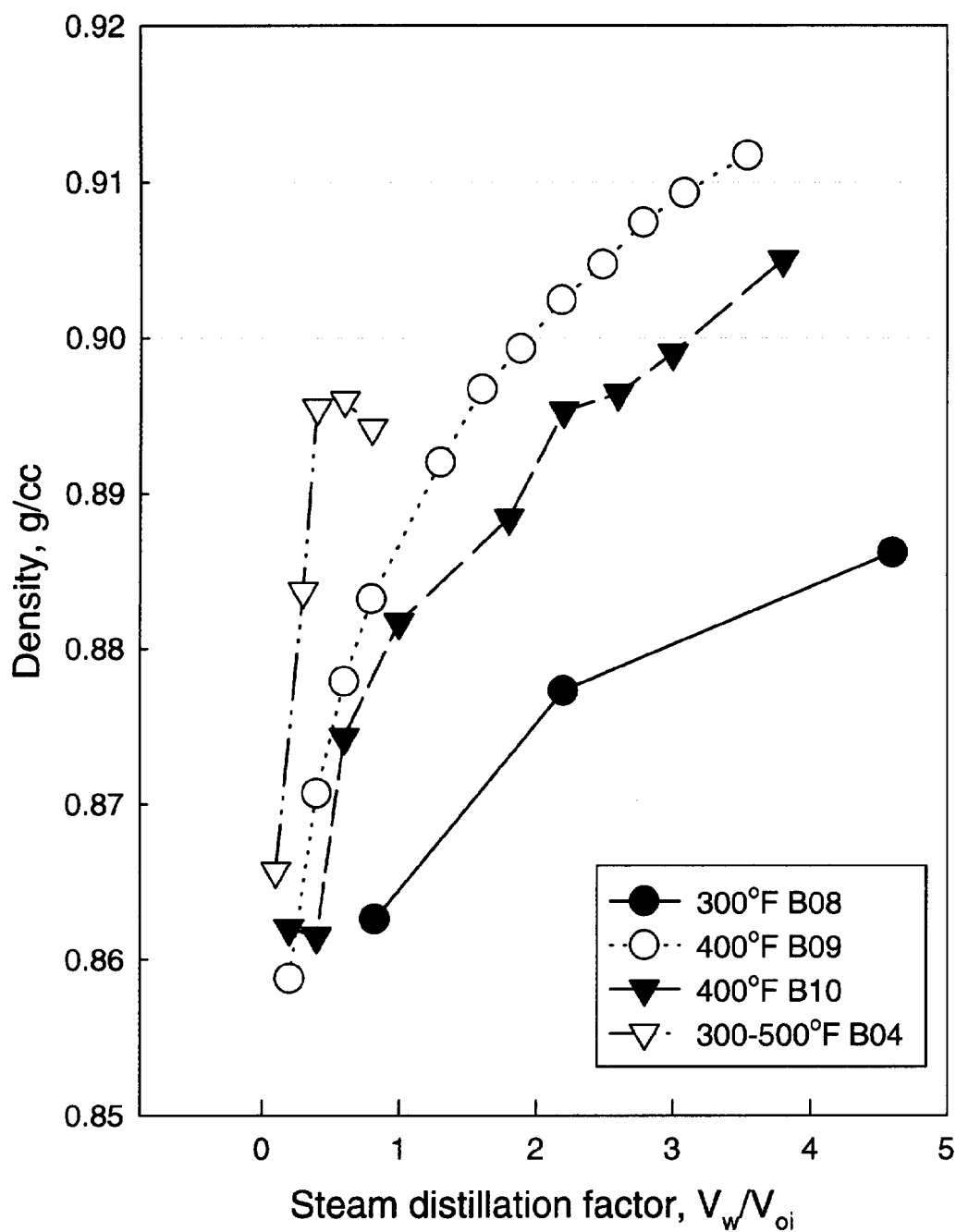


Fig. 9--Summary of distillate densities from Kern River steam distillation tests.

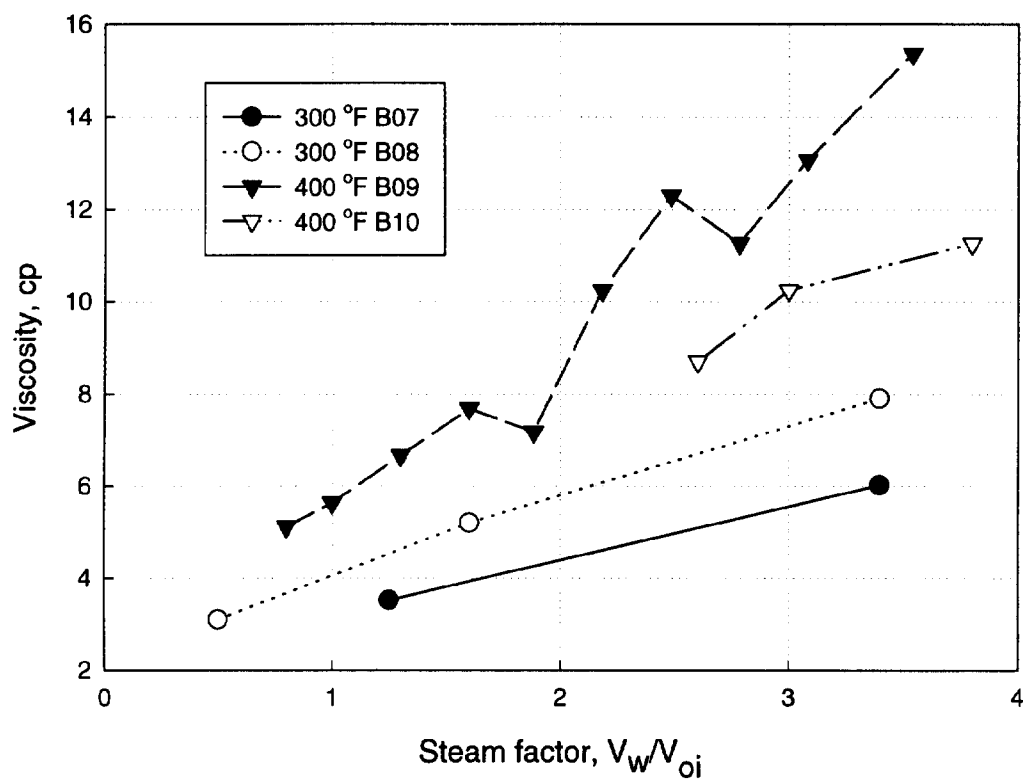


Fig. 10—Ambient temperature distillate viscosities with steam throughput for overheads from 300 and 400°F steam distillations.

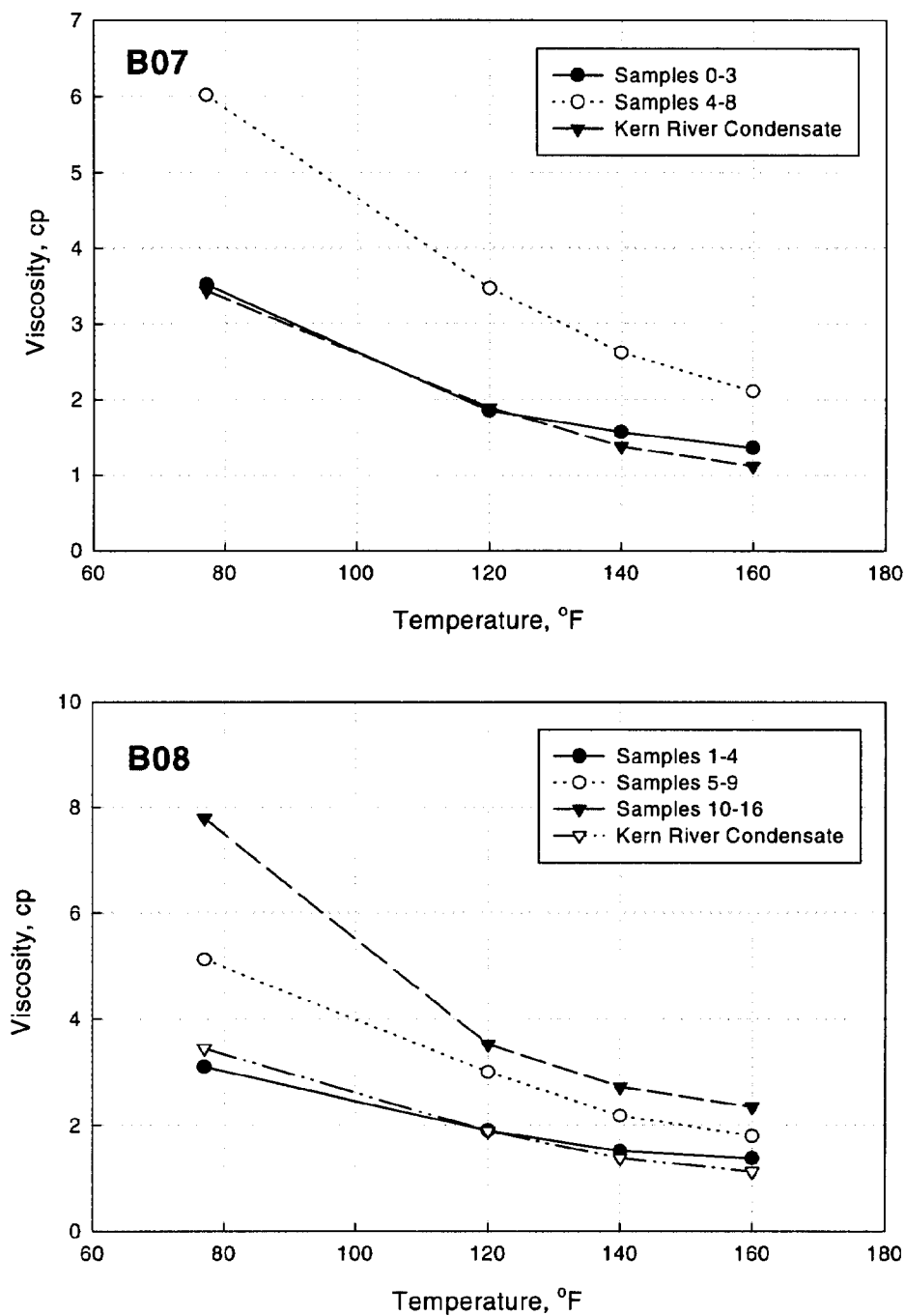


Fig. 11--Viscosity with temperature measurements of Kern River 300 °F overheads.

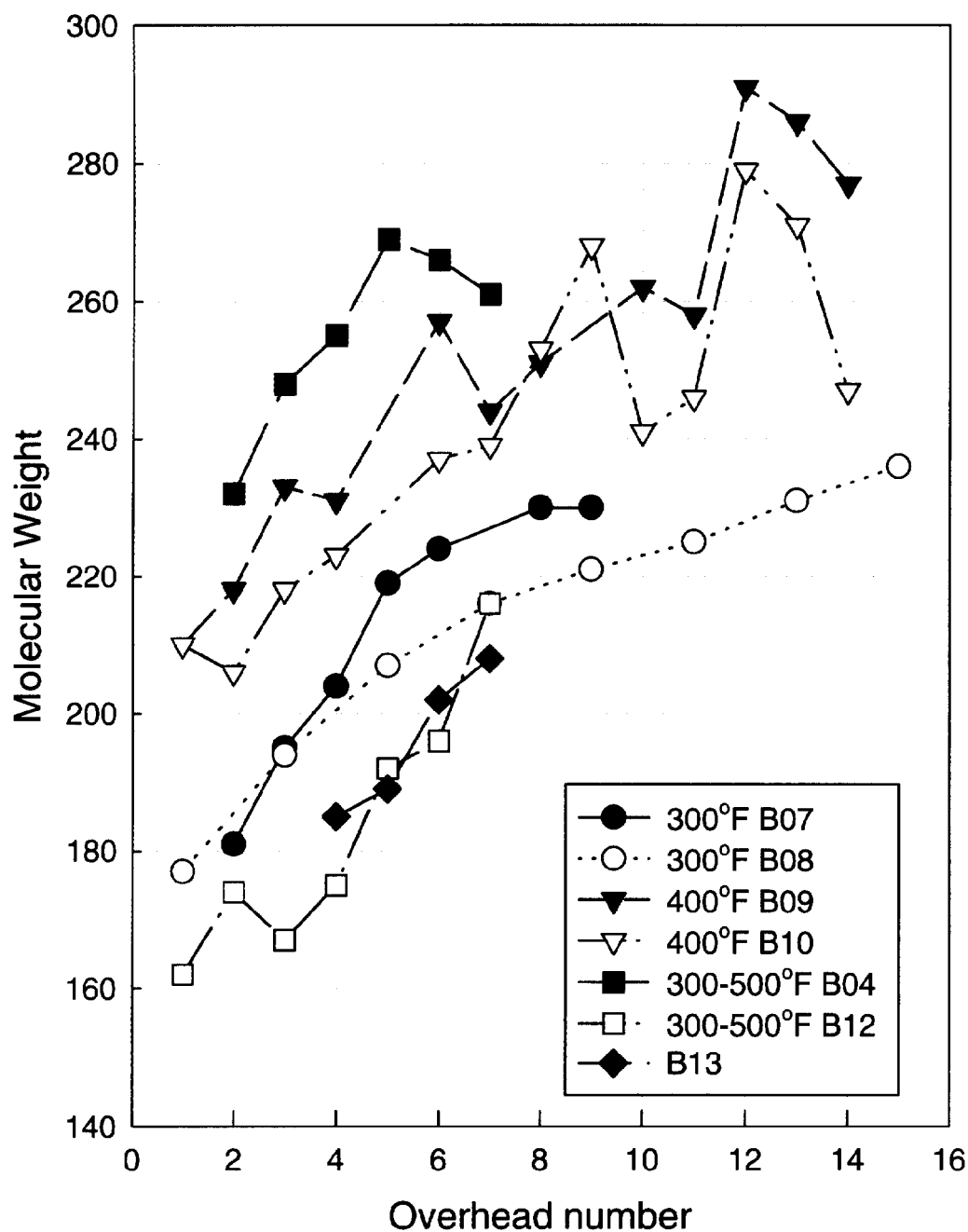


Fig. 12—Summary of molecular weights of distillates from steam distillation tests.

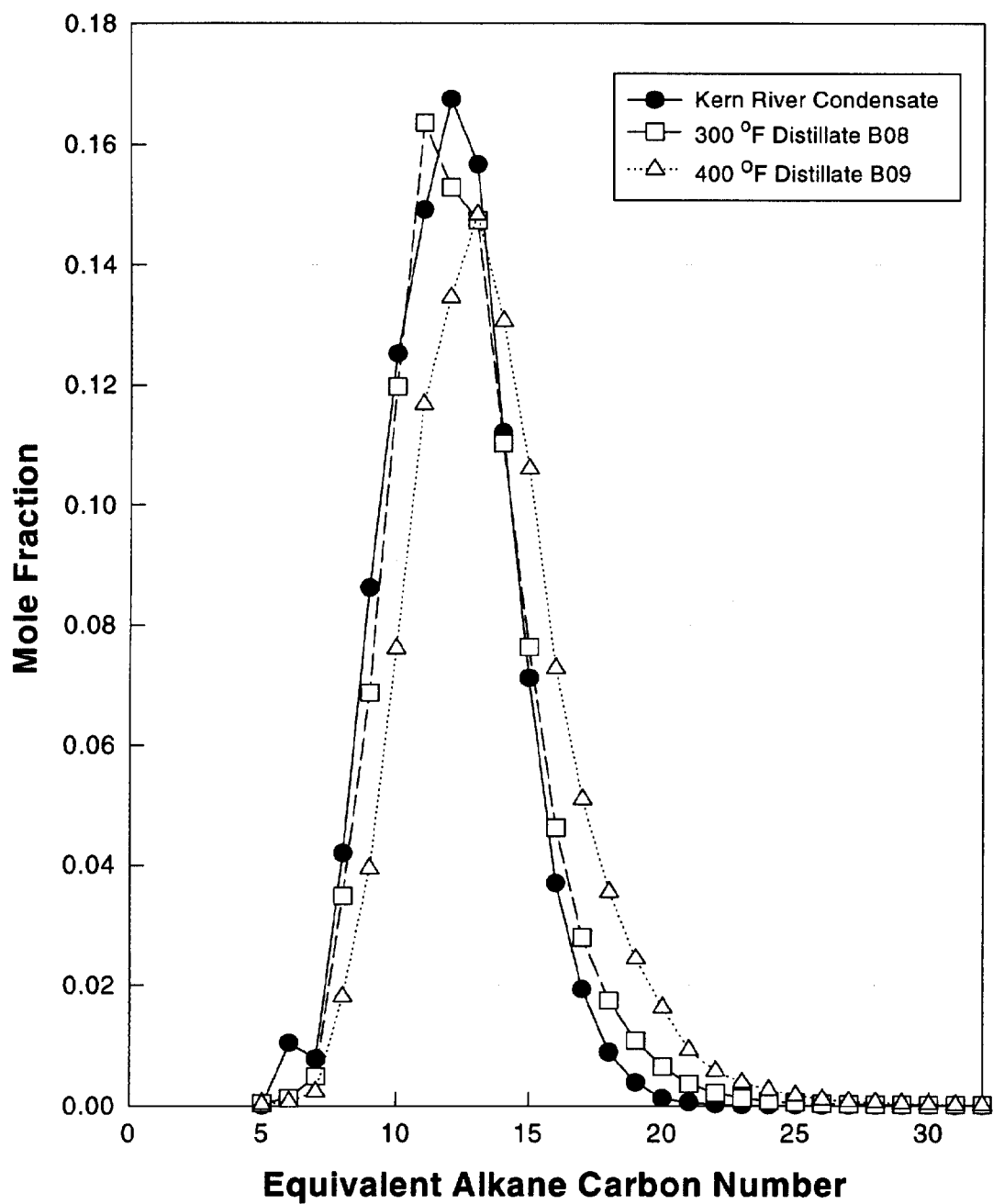


Fig. 13—Hydrocarbon distribution of Kern River condensate and overheads from steam distillation runs distribution of Kern River condensate and overheads from steam distillation runs.